Solvent and Temperature Effect on Chiral Conformation of Poly(*meta*-benzamide)s

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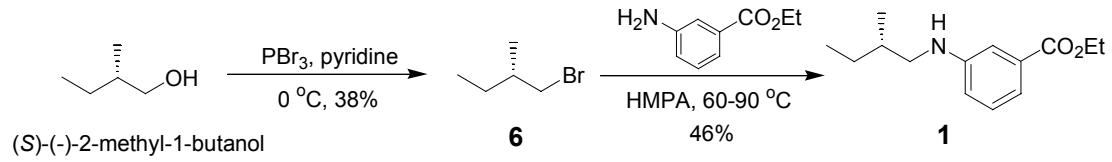
Supporting Information

General. ^{1}H and ^{13}C NMR spectra were obtained on JEOL ECA-500 and ECA-600 spectrometers, and the internal standards of ^{1}H and ^{13}C NMR spectra were tetramethylsilane (0.00 ppm) and midpoint of $CDCl_3$ (77.0 ppm), respectively. IR spectra were recorded on a JASCO FT/IR-410. Column chromatography was performed on silica gel (Kieselgel 60, 230–400 mesh, Merck) with a specified solvent. Commercially available (Kanto) dehydrated tetrahydrofuran (THF, stabilizer-free) was used as a dry solvent. The M_n and M_w/M_n values of polymers were measured on a Shodex GPC-101 equipped with Shodex UV-41, Shodex RI-71S, and two Shodex KF-804L columns (bead size = 7 μm, pore size = 200 Å). THF was used as the eluent (temperature = 40 °C, flow rate = 2 mL/min). Calibration was carried out using polystyrene standards. Isolation of polyamides was carried out with a Japan Analytical Industry LC-908 Recycling Preparative HPLC (eluent: chloroform) using two TSK-gel columns (2 × G2000H_{HR}). UV-vis spectra were measured on a Hitachi U-3300 spectrophotometer and a JASCO V-550 spectrometer. CD spectra were measured on JASCO J-600 and J-820 spectropolarimeters using a 10 mm quartz cell. The concentration of each solution for UV and CD experiments was adjusted so that the absorbance of the monomers or the polymers was 1 at 250 nm for **1**-**4** and poly**1**-**4** in chloroform and water, and for **3**, **4**, poly**3**, and poly**4** in methanol, or at 260 nm for **1**, **2**, poly**1**, and poly**2** in methanol.

Synthesis of monomer 1. The monomer **1** was synthesized by the procedure as shown in Scheme S1.

Scheme S1

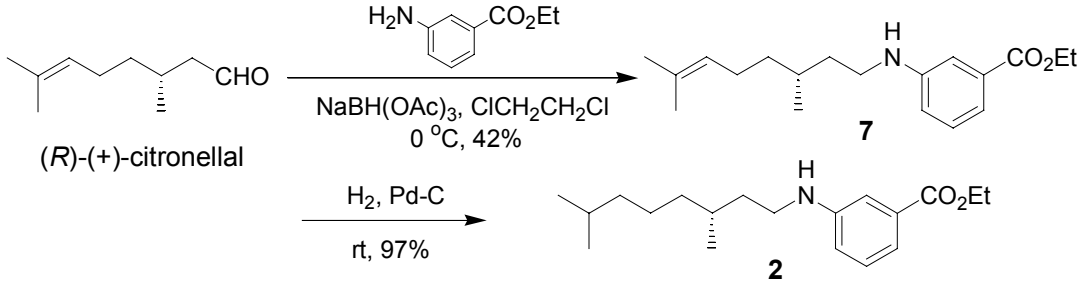


Synthesis of 6.[1] PBr_3 (1.94 mL, 20.4 mmol) was added dropwise to a mixture of (*S*)-(–)-2-methyl-1-butanol (5.01 g, 56.8 mmol) and pyridine (1.5 mL, 18 mmol) at 0 °C, and the whole was stirred at 0 °C for 2 h under an Ar atmosphere. Distillation (80 °C/10 mmHg) of the reaction mixture gave a crude product as a distillate, which was diluted with *n*-pentane. The solution was washed with 5% NaOH, 10% H_2SO_4, and water, and dried over $CaCl_2$. After removal of pentane at atmospheric pressure, the residue was distilled to give **6** as a colorless oil (2.95 g, 38%): bp 118–120 °C (lit.[2] 118–120 °C); ^{1}H NMR (500 MHz, $CDCl_3$) δ 3.40 (dd, J = 9.9 and 5.0 Hz, 1 H), 3.33 (dd, J = 9.7 and 6.3 Hz, 1 H), 1.72 (oct, J = 6.0 Hz, 1 H), 1.54–1.45 (m, 1 H), 1.32–1.24 (m, 1 H), 1.01 (d, J = 6.9 Hz, 3 H), 0.91 (t, J = 7.6 Hz, 3 H).

Synthesis of 1. Ethyl 3-aminobenzoate (3.0 mL, 20 mmol) was added to a solution of **6** (2.01 g, 13.3 mmol) in hexamethylphosphoric triamide (HMPA, 10 mL). The mixture was stirred under an Ar atmosphere at 60 °C for 2 h and then at 90 °C for 22 h, and poured into saturated aqueous $NaHCO_3$. The mixture was extracted with ether, and the organic layer was washed with water and brine, dried over $MgSO_4$, and evaporated. The residue was purified by silica gel column chromatography (AcOEt/hexane = 1/10) to give **1** as a yellow viscous oil (1.45 g, 46%): ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.34 (d, J = 7.6 Hz, 1 H), 7.26 (m, 1 H), 7.21 (t, J = 7.9 Hz, 1 H), 6.76 (dd, J = 8.1 and 2.5 Hz, 1 H), 4.35 (q, J = 7.2 Hz, 2 H), 3.80 (br s, 1 H), 3.09 (dd, J = 12.4 and 6.2 Hz, 1 H), 2.93 (dd, J = 12.3 and 7.2 Hz, 1 H), 1.67 (oct, J = 6.5 Hz, 1 H), 1.53–1.47 (m, 1 H), 1.38 (t, J = 7.2 Hz, 3 H), 1.27–1.20 (m, 1 H), 0.98 (d, J = 6.9 Hz, 3 H), 0.94 (t, J = 7.6 Hz, 3 H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 160.1, 141.6, 124.3, 122.0, 111.0, 109.8, 106.2, 53.8, 42.8, 27.4, 20.2, 10.5, 7.3, 4.3; IR (neat) 2961, 2930, 2874, 1606, 1514, 1490, 1474, 1367, 1334, 753, 684 cm^{-1}.

Synthesis of monomer 2. The monomer **2** was synthesized by the procedure as shown in Scheme S2.

Scheme S2



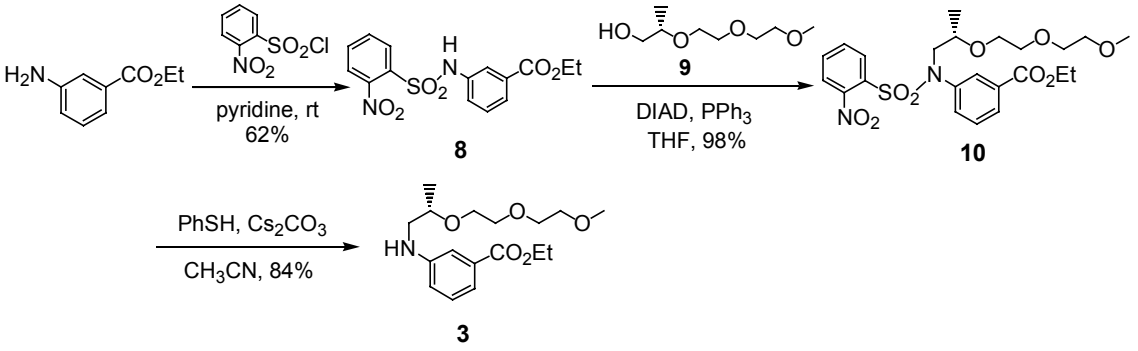
Synthesis of 7.[3] $NaBH(OAc)_3$ (3.22 g, 15.2 mmol) was added to a solution of (*R*)-(+)-citronellal (2.00 g, 13.0 mmol) and ethyl 3-aminobenzoate (2.0 mL, 13 mmol) in 1,2-dichloroethane (45 mL) at 0 °C. After stirred at 0 °C for 3 h under an Ar atmosphere, the reaction mixture was neutralized with saturated $NaHCO_3$ and extracted with AcOEt. The organic layer was washed with water and brine, dried over $MgSO_4$, and evaporated. The residue was purified by silica gel column chromatography (AcOEt/hexane = 1/10) to give **7** as a pale yellow oil (1.66 g, 42%): ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.35 (dt, J = 7.7 and 1.2 Hz, 1 H), 7.26 (m, 1 H), 7.21 (t, J = 7.9 Hz, 1 H), 6.76 (ddd, J = 8.0, 2.6, and 1.0 Hz, 1 H), 5.10 (t, J = 7.2 Hz, 1 H), 4.35 (q, J = 7.2 Hz, 2 H), 3.68 (br s, 1 H), 3.20–3.11 (m, 2 H), 2.02–1.95 (m, 2 H), 1.69–1.56 (m, 10 H), 1.48–1.35 (m, 5 H), 1.25–1.19 (m, 1 H), 0.95 (d, J = 6.5 Hz, 3 H); ^{13}C NMR (126 Hz, $CDCl_3$) δ 167.1, 148.5, 131.4, 129.1, 124.6, 118.2, 117.0, 113.3, 60.8, 41.9, 37.1, 36.6, 30.4, 25.7, 25.5, 19.6, 17.7, 14.4; IR (neat) 2966, 2926, 1670, 1609, 1366, 1333, 1239, 1105, 752, 685 cm^{-1}.

Synthesis of 2. A catalytic amount of 5% Pd-C (0.35 g) was added to a solution of **7** (1.30 g, 4.29 mmol) in AcOEt (200 mL), and hydrogenation was carried out at room temperature for 3 h under a H_2 atmosphere with vigorous stirring. The reaction mixture was filtered and evaporated, and the residue was purified by silica gel column chromatography (AcOEt/hexane = 1/10) to give **2** as a pale yellow viscous oil (1.27 g, 97%). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.35 (dt, J = 7.9 and 1.2 Hz, 1 H), 7.26 (m, 1 H), 7.21 (t, J = 7.9 Hz, 1 H), 6.76 (ddd, J = 7.9, 2.4, and 1.0 Hz, 1 H), 4.35 (q, J = 7.2 Hz, 2 H), 3.67 (br s, 1 H), 3.20–3.10 (m, 2 H), 1.67–1.62 (m, 1 H), 1.57–1.51 (m, 2 H), 1.49–1.41 (m, 1 H), 1.39–1.23 (m, 6 H), 1.18–1.12 (m, 3 H), 0.94 (d, J = 6.9 Hz, 3 H), 0.87 (d, J = 6.9 Hz, 6 H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 167.1, 148.5, 131.4, 129.0,

118.2, 117.0, 113.3, 60.8, 41.9, 39.2, 37.2, 36.7, 30.8, 28.0, 24.7, 22.7, 22.6, 19.7, 14.3; IR (neat) 2955, 2926, 2869, 1707, 1366, 1334, 1240, 1106, 752, 684 cm^{-1}.

Synthesis of monomer 3. The monomer **3** was synthesized by the procedure as shown in Scheme S3.

Scheme S3



Synthesis of 8. To a solution of ethyl 3-aminobenzoate (4.72 g, 28.6 mmol) in pyridine (30 mL) was added 2-nitrobenzenesulfonyl chloride (7.00 g, 31.6 mmol) at 0 °C. The mixture was stirred at room temperature for 2.5 h, and poured into 2 M HCl (135 mL). The aqueous layer was extracted with CH_2Cl_2 and the organic layer was washed with brine, dried over $MgSO_4$, and evaporated. The residue was purified by silica gel column chromatography (AcOEt/hexane = 1/1) to give **8** as a light brown solid (6.19 g, 62%): ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.89–7.85 (m, 3 H), 7.80 (t, J = 1.9 Hz, 1 H), 7.71 (td, J = 7.7 and 1.4 Hz, 1 H), 7.60 (td, J = 7.7 and 1.4 Hz, 1 H), 7.48 (ddd, J = 8.0, 2.3, and 1.1 Hz, 1 H), 7.42 (br s, 1 H), 7.38 (t, J = 7.9 Hz, 1 H), 4.36 (q, J = 7.1 Hz, 2 H), 1.37 (t, J = 7.3 Hz, 3 H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 165.6, 135.8, 134.1, 132.7, 132.1, 131.9, 131.7, 129.6, 127.5, 127.3, 125.5, 123.8, 61.4, 14.2; IR (KBr) 3084, 1592, 1537, 1420, 1360, 782, 752 cm^{-1}.

Synthesis of 10. Diisopropyl azodicarboxylate (DIAD, 40% in toluene, 3.8 mL, 7.1 mmol) was added to a solution of **8** (1.91 g, 5.46 mmol), **9**[4] (0.667 g, 3.74 mmol), and PPh_3 (1.65 g, 6.29 mmol) in dry THF (20 mL) at 0 °C under an Ar atmosphere. The mixture was stirred at room temperature for 13 h, and concentrated under reduced pressure. The residue was purified by silica gel column chromatography (AcOEt/hexane = 1/1) to give **10** as a yellow viscous oil (1.87 g, 98%): ^{1}H NMR (500 MHz, $CDCl_3$) δ

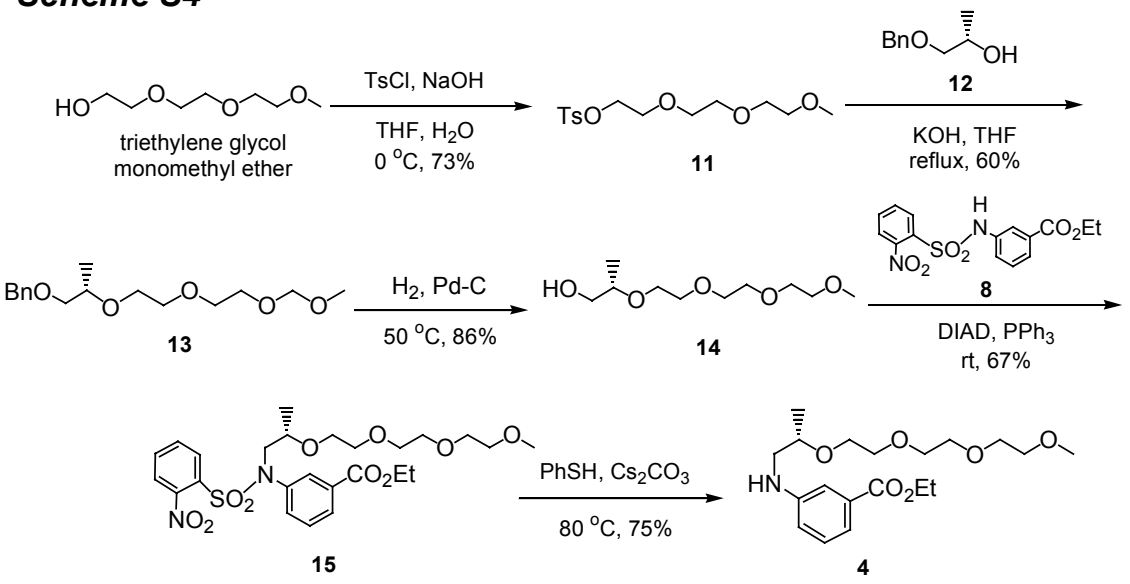
7.97 (dt, J = 7.7 and 1.4 Hz, 1 H), 7.83 (t, J = 1.9 Hz, 1 H), 7.64 (td, J = 7.6 and 1.4 Hz, 1 H), 7.60 (dd, J = 8.0 and 1.4 Hz, 1 H), 7.55 (ddd, J = 8.0, 2.3, and 1.1 Hz, 1 H), 7.51 (dd, J = 7.9 and 1.4 Hz, 1 H), 7.46 (td, J = 7.0 and 1.4 Hz, 1 H), 7.40 (t, J = 7.9 Hz, 1 H), 4.35 (q, J = 7.2 Hz, 2 H), 3.86 and 3.82 (ABq, J = 14.5 Hz, each part d with J = 6.7 and 5.0 Hz, 2 H), 3.64–3.50 (m, 4 H), 3.50–3.45 (m, 4 H), 3.43–3.40 (m, 1 H), 3.36 (s, 3 H), 1.37 (t, J = 7.2 Hz, 3 H), 1.20 (d, J = 6.0 Hz, 3 H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 165.5, 139.5, 134.2, 133.7, 131.9, 131.8, 131.1, 129.9, 129.2, 123.9, 74.7, 71.9, 70.5, 68.1, 61.3, 57.0; IR (neat) 2979, 2877, 1586, 1546, 1369, 1108, 765, 695 cm^{-1}.

Synthesis of 3. A solution of benzenethiol (0.380 g, 3.45 mmol) in CH_3CN (10 mL) and Cs_2CO_3 (3.16 g, 9.68 mmol) were added to a solution of **10** (1.68 g, 3.30 mmol) in CH_3CN (70 mL). The reaction mixture was stirred at 80 ^{o}C for 1.5 h, allowed to cool to room temperature, and poured into water. The mixture was extracted with CH_2Cl_2. The organic layer was washed with water, dried over $MgSO_4$, and evaporated. The residue was purified by silica gel column chromatography (AcOEt/hexane = 2/1, then 1/1) to give **3** as a yellow oil (0.904 g, 84%): ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.36 (dt, J = 7.5 and 1.3 Hz, 1 H), 7.26 (t, J = 2.0 Hz, 1 H), 7.21 (t, J = 7.9 Hz, 1 H), 6.81 (ddd, J = 8.1, 2.5, and 1.1 Hz, 1 H), 4.47 (br s, 1 H), 4.35 (q, J = 7.2 Hz, 2 H), 3.78–3.72 (m, 2 H), 3.68–3.62 (m, 4 H), 3.60–3.53 (m, 3 H), 3.39 (s, 3 H), 3.27 (dd, J = 12.7 and 3.2 Hz, 1 H), 3.07 (dd, J = 12.6 and 7.7 Hz, 1 H), 1.38 (t, J = 7.2 Hz, 3 H), 1.24 (d, J = 6.3 Hz, 3 H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 167.1, 148.5, 131.2, 129.0, 118.3, 74.2, 71.9, 70.7, 70.5, 67.9, 60.7, 59.0, 49.0, 17.8, 14.3; IR (neat) 2978, 2932, 2874, 2368, 1606, 1105, 754 cm^{-1}.

Synthesis of monomer 4. The monomer **4** was synthesized by the procedure as shown in Scheme S4.

Synthesis of 11. NaOH (3.86 g, 96.4 mmol) and triethylene glycol monomethyl ether (12.4 g, 75.6 mmol) in a mixture of water (40 mL) and THF (45 mL) was stirred at 0 ^{o}C. *p*-Toluenesulfonyl chloride (12.0 g, 63.0 mmol) in THF (45 mL) was added dropwise to the mixture. The solution was stirred at 0 ^{o}C for 1.5 h, then poured into ice-water, and the mixture was extracted with CH_2Cl_2. The organic layer was washed with brine, dried over $MgSO_4$ and evaporated, and the residue was purified by silica gel column chromatography (AcOEt/hexane = 2:1) to give **11** as a colorless oil (14.6 g,

Scheme S4



73%): ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.80 (d, J = 8.3 Hz, 2 H), 7.34 (d, J = 8.0 Hz, 2 H), 4.16 (t, J = 4.9 Hz, 2 H), 3.69 (t, J = 4.9 Hz, 2 H), 3.62–3.58 (m, 6 H), 3.53 (dd, J = 6.3 and 3.2 Hz, 2 H), 3.37 (s, 3 H), 2.45 (s, 3 H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 144.8, 133.0, 129.8, 127.9, 71.9, 70.7, 70.51, 70.50, 69.2, 68.6, 59.0, 21.6; IR (neat) 2925, 2879, 1356, 1177, 818 cm^{-1}.

Synthesis of 13. A solution of **12**[4] (6.01 g, 36.1 mmol), **11** (23.0 g, 72.4 mmol) and KOH (6.91 g, 123 mmol) in dry THF (95 mL) was stirred under reflux for 17 h under an Ar atmosphere, allowed to cool to room temperature, and poured into water. The mixture was extracted with CH_2Cl_2. The organic layer was washed with water, dried over $MgSO_4$, and evaporated. The residue was purified by distillation (135.0–150.5 ^{o}C/0.18 mmHg) followed by silica gel column chromatography (AcOEt/hexane = 1/1) to give **13** as a pale yellow oil (6.96 g, 60%): ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.36–7.27 (m, 5 H), 4.57 (d, J = 4.6 Hz, 2 H), 3.71–3.62 (m, 11 H), 3.56–3.53 (m, 1 H), 3.51 (dd, J = 10.0 and 6.0 Hz, 1 H), 3.41 (dd, J = 10.0 and 6.0 Hz, 1 H), 3.37 (s, 3 H), 1.17 (d, J = 6.3 Hz, 3 H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 138.4, 128.3, 127.6, 127.5, 75.0, 74.0, 73.2, 71.9, 70.8, 70.6, 70.52, 70.45, 68.5, 59.0, 17.2; IR (neat) 2979, 2925, 2865, 1638, 1373, 741, 704 cm^{-1}.

Synthesis of 14. The benzyl ether **13** (1.22 g, 3.89 mmol) was dissolved in ethanol (13 mL) and acidified with 37% HCl (0.1 mL). A catalytic amount of 5% Pd/C (0.157 g) was added to the solution, and hydrogenation was carried out under a H_2 atmosphere

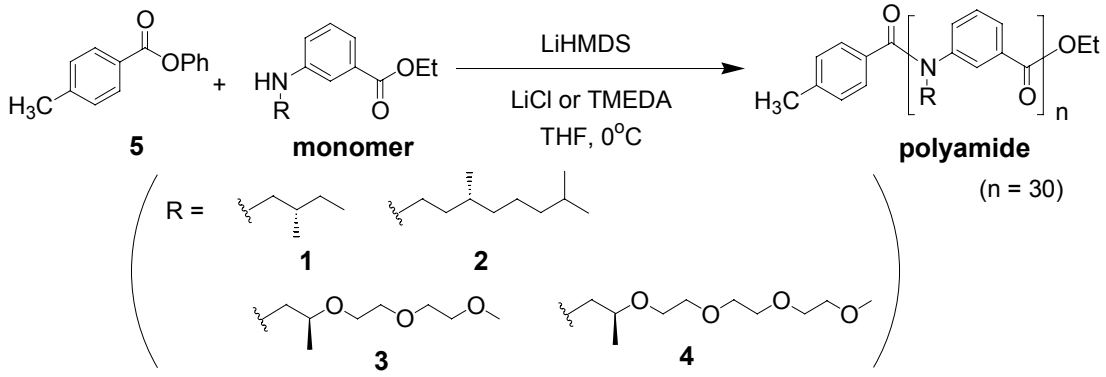
with vigorous stirring at 50 °C for 1 h. The reaction mixture was filtered and evaporated, and the residue was purified by silica gel column chromatography (AcOEt) to give **14** as a pale yellow oil (0.751 g, 86%): ^{1}H NMR (500 MHz, $CDCl_3$) δ 3.79–3.76 (m, 1 H), 3.69–3.55 (m, 14 H), 3.46 (dd, J = 11.6 and 7.5 Hz, 1 H), 3.39 (s, 3 H), 1.11 (d, J = 6.3 Hz, 3 H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 71.8, 70.8, 70.39, 70.38, 70.3, 67.9, 66.2, 58.9, 16.0; IR (neat) 3435, 2930, 2887, 1646, 1093 cm^{-1}.

Synthesis of 15. Coupling reaction between **14** and **8** was carried out in the same manner as the synthesis of **10**. Purification by silica gel column chromatography (AcOEt/hexane = 3/1, and then CH_2Cl_2/AcOEt = 1/1) gave **15** as a viscous light brown oil (67%): ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.97 (dt, J = 7.7 and 1.3 Hz, 1 H), 7.83 (t, J = 1.9 Hz, 1 H), 7.64 (td, J = 7.6 and 1.4 Hz, 1 H), 7.60 (dd, J = 8.0 and 1.7 Hz, 1 H), 7.55 (ddd, J = 7.8, 2.2, and 1.1 Hz, 1 H), 7.51 (dd, J = 8.0 and 1.4 Hz, 1 H), 7.47 (td, J = 7.5 and 1.5 Hz, 1 H), 7.41 (t, J = 7.9 Hz, 1 H), 4.35 (q, J = 7.2 Hz, 2 H), 3.86 and 3.82 (ABq, J = 14.6 Hz, each part d with J = 6.9 and 5.2 Hz, 2 H), 3.63–3.47 (m, 12 H), 3.45–3.39 (m, 1 H), 3.37 (s, 3 H), 1.37 (t, J = 7.2 Hz, 3 H), 1.19 (d, J = 6.9 Hz, 3 H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 165.4, 148.0, 139.5, 134.2, 133.7, 131.84, 131.75, 131.1, 129.9, 129.3, 129.2, 74.7, 71.9, 70.53, 70.49, 70.45, 68.1, 61.3, 59.0, 57.0, 17.3, 14.2; IR (neat) 2984, 2933, 1638, 1364, 1281, 1168, 768, 699 cm^{-1}.

Synthesis of 4. The 2-nitrobenzenesulfonyl group of **15** was removed in the same manner as the preparation of **3**. Purification by silica gel column chromatography (AcOEt/hexane = 3/1) followed by preparative HPLC gave **4** as a yellow oil (75%): ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.36 (dt, J = 7.8 and 1.3 Hz, 1 H), 7.27–7.26 (m, 1 H), 7.20 (t, J = 7.9 Hz, 1 H), 6.80 (ddd, J = 8.0, 2.6, and 0.9 Hz, 1 H), 4.49 (br s, 1 H), 4.35 (q, J = 7.1 Hz, 2 H), 3.77–3.72 (m, 2 H), 3.69–3.64 (m, 8 H), 3.59–3.50 (m, 3 H), 3.37 (s, 3 H), 3.27 (dd, J = 12.6 and 3.2 Hz, 1 H), 3.07 (dd, J = 12.6 and 7.7 Hz, 1 H), 1.38 (t, J = 7.2 Hz, 3 H), 1.24 (d, J = 6.3 Hz, 3 H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 167.1, 148.5, 131.3, 129.0, 118.3, 117.6, 113.3, 74.2, 71.9, 70.8, 70.6, 70.54, 70.50, 67.9, 60.7, 59.0, 49.0, 17.8, 14.3; IR (neat) 2976, 2873, 2246, 1715, 1105, 755 cm^{-1}.

Synthesis of Poly1-4. Poly**1**-**4** were synthesized by the procedure as shown in Scheme S5. All glass apparatuses were dried prior to use. Addition of reagents into the reaction flask was carried out via a syringe from the three-way stopcock with a stream of nitrogen.

Scheme S5



Synthesis of poly1. LiCl (0.119 g, 2.81 mmol) was placed in a flask equipped with a three-way stopcock, and dried at 250 °C under reduced pressure. The flask was cooled to room temperature under an Ar atmosphere, and then charged with dry THF (0.60 mL) and 1 M solution of LiHMDS in THF (0.60 mL, 0.60 mmol). The flask was cooled to 0 °C with stirring. Into the flask was added a solution of **5** (0.0035 g, 0.017 mmol) in dry THF (0.25 mL), followed by a solution of **1** (0.119 g, 0.504 mmol) in dry THF (0.60 mL) dropwise over ca. 45 min (when reddish color of the reaction mixture disappeared, the next drop of the solution was added) at 0 °C with stirring. The reaction mixture was stirred at 0 °C for 1 h, quenched with saturated NH_4Cl, and extracted with CH_2Cl_2. The organic layer was dried over $MgSO_4$ and evaporated. The residue was purified by preparative HPLC (eluent: $CHCl_3$) using polystyrene gel column to give poly**1** as a off-white solid (90%): ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.11–7.03 (m, 1 H), 6.93–6.76 (m, 2 H), 6.64 (br s, 1 H), 3.58 (m, 2 H), 1.50–1.41 (m, 1 H), 1.39–1.26 (m, 1 H), 1.15–1.07 (m, 1 H), 0.88–0.80 (m, 6 H); IR (KBr) 2962, 2928, 2875, 1654, 748 cm^{-1}.

Poly2. Pale yellow solid (68%): ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.17–7.05 (m, 1 H), 6.86–6.71 (m, 2 H), 6.60 (br s, 1 H), 3.86–3.39 (m, 2 H), 1.53 (m, 1 H), 1.39–1.06 (m, 9 H), 0.90–0.83 (m, 9 H); IR (KBr) 2954, 2926, 2869, 1654, 749 cm^{-1}.

Synthesis of poly3. A flask, equipped with a three-way stopcock, was purged with Ar and then charged with dry THF (0.60 mL), 1 M solution of LiHMDS in THF (0.60 mL, 0.60 mmol), and TMEDA (0.35 mL, 2.3 mmol). The flask was cooled to 0 °C with stirring. Into the flask was added a solution of **5** (0.0028 g, 0.013 mmol) in dry THF (0.20 mL), followed by a solution of **3** (0.131 g, 0.402 mmol) in dry THF (0.50 mL) dropwise over ca. 40 min (when reddish color of the reaction mixture disappeared, the

next drop of the solution was added) at 0 °C with stirring. The reaction mixture was stirred at 0 °C for 22 h, quenched with saturated NH_4Cl, and extracted with CH_2Cl_2. The organic layer was dried over $MgSO_4$ and evaporated. The residue was purified by preparative HPLC (eluent: $CHCl_3$) using polystyrene gel column to give poly**3** as a viscous off-white solid (10%): ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.43–7.10 (m, 1 H), 6.95–6.47 (m, 3 H), 3.73–3.43 (m, 11 H), 3.34–3.33 (m, 3 H), 1.19–0.97 (m, 3 H); IR (KBr) 2969, 2875, 1648, 1103, 755 cm^{-1}.

Poly4. Viscous light brown solid (44%): ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.50–7.18 (m, 1 H), 7.00–6.38 (m, 3 H), 3.99–3.43 (m, 15 H), 3.39–3.35 (m, 3 H), 1.18–0.93 (m, 3 H); IR (KBr) 2965, 2928, 2874, 1648, 1107, 754 cm^{-1}.

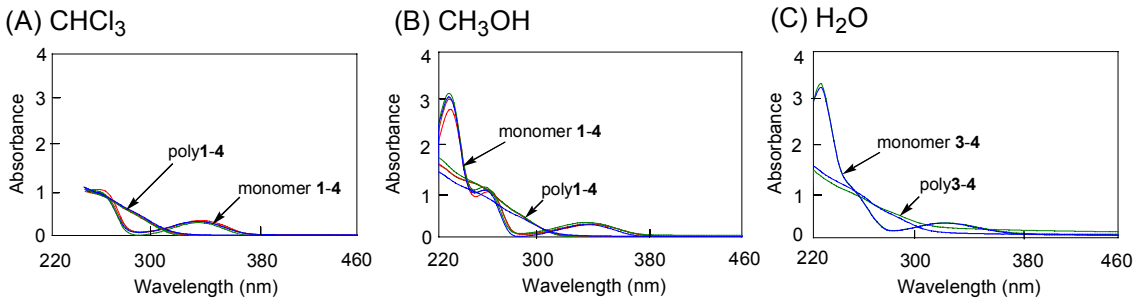


Figure S1. UV spectra of **1** and poly**1** (red line), **2** and poly**2** (brown line), **3** and poly**3** (green line), and **4** and poly**4** (blue line) in (A) $CHCl_3$, (B) CH_3OH, and (C) H_2O.

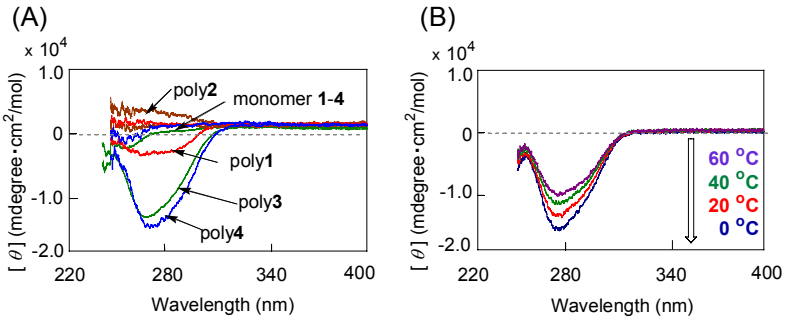


Figure S2. (A) CD spectra of **1** and poly**1** (red line), **2** and poly**2** (brown line), **3** and poly**3** (green line), and **4** and poly**4** (blue line) in $CHCl_3$ at 25 °C. (B) CD spectra of poly**4** in $CHCl_3$ at 0 °C (blue line), 20 °C (red line), 40 °C (green line), and 60 °C (violet line). The CD study in $CHCl_3$ was limited due to the absorption of $CHCl_3$ below 250 nm.

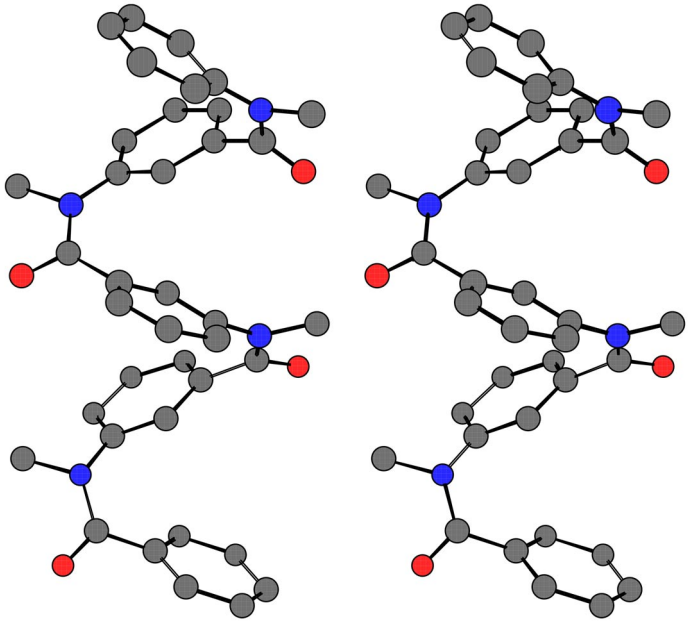


Figure S3. Stereoview of the proposed helical conformation of 3-(methylamino)benzoic acid pentamer with the anti arrangement. Hydrogen atoms and terminal amino and carbonyl groups are omitted for clarity.

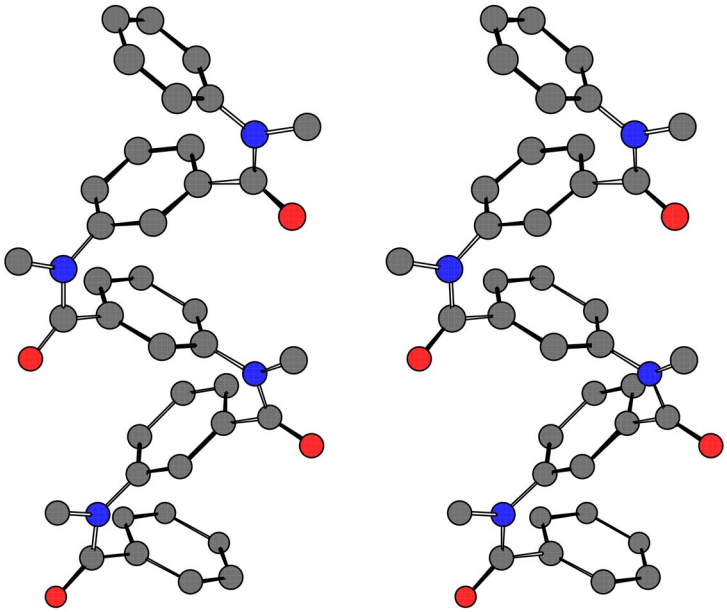


Figure S4. Stereoview of the proposed zigzag conformation of 3-(methylamino)benzoic acid pentamer with the anti arrangement. Hydrogen atoms and terminal amino and carbonyl groups are omitted for clarity.

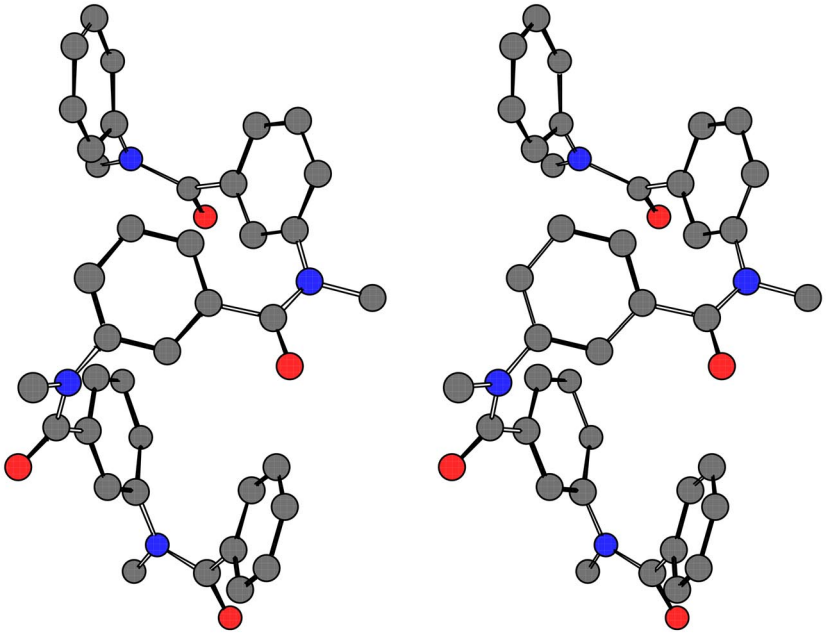


Figure S5. Stereoview of the proposed helical conformation of 3-(methylamino)benzoic acid pentamer with the syn arrangement. Hydrogen atoms and terminal amino and carbonyl groups are omitted for clarity.

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